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STUDY OF GROWTH PARAMETERS FOR  
REFRACTORY CARBIDE SINGLE CRYSTALS

By: F. A. Halden

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A. E. Gorum  
A. E. Gorum, Director  
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## I INTRODUCTION

Interest in the super refractory compounds--particularly the carbides--has increased considerably in the last five years as a result of an increasing number of potential applications for structural materials at temperatures above 2000<sup>o</sup> C. Unfortunately, very little reliable information is available to assist in evaluation of these materials. Their purity is generally poor; dense, uniform shapes are difficult to fabricate; and good single crystals are almost nonexistent. For these reasons, the information we have is highly suspect, and one can only guess at ultimate properties or the influence of stoichiometry, structure, and purity on properties.

To obtain many of the data that will ultimately be required, well-characterized single crystals will be needed. For this reason, a program has been initiated by the National Aeronautics and Space Administration at Stanford Research Institute to investigate suitable growth techniques and critical process parameters for preparation of single crystals of refractory transition metal carbides. The specific objectives of this study are:

1. To determine the feasibility of, and procedures for applying, recently developed liquid metal solution crystal growth techniques and new heating methods for Verneuil crystal growth, for preparation of refractory carbide single crystals
2. To grow, using the most promising technique, single crystals of refractory carbides and to characterize these crystals
3. To establish the feasibility of controlling crystal stoichiometry and structure by modifications in the crystal growth environment.

## II SUMMARY AND CONCLUSIONS

During the first quarter of this program, a major effort was devoted to examining the literature for information on phase diagram relationships, structural modifications introduced by stoichiometry changes, the thermodynamics of the carbides and potential gaseous environmental species, and the solubility of the carbides in metal alloy melts.

Several modifications were made on the r-f plasma generator in order to provide the degree of operational stability that is required for crystal growth. Furnaces have been designed for initial studies in which both plasma and a-c arc-melting techniques will be used. These furnaces are being constructed.

Solution studies have been delayed until a new furnace, being constructed with SRI funds, is placed in operation. This delay is prompted by a desire to avoid contamination that would occur if a single furnace was used for studies on widely differing crystal compositions. At present, electronic-grade silicon carbide crystals, many doped with boron or aluminum, are being grown in this furnace, and introduction of trace amounts of hafnium or tantalum would be quite detrimental. Likewise, the presence of silicon, boron, or aluminum in the other furnace would be undesirable in attempting to grow hafnium and tantalum carbide crystals.

### III EXPERIMENTAL STUDIES AND DISCUSSION

The chemical compositions under investigation are hafnium carbide (HfC), tantalum carbide (TaC), and solid solutions of these compounds.

Since it is desired, through this program, to obtain large single crystals suitable for structural studies, work will be limited, initially at least, to melt and solution growth techniques in which nucleation procedures appear to be relatively straightforward. It is anticipated that, in attempting to grow crystals of the carbides, improper control over any stage in material handling will lead to failure in crystal growth. Unfortunately, failure to obtain crystals frequently provides no clue as to why they did not form. For this reason, it is essential that each step in crystal growth be carefully controlled. This includes: (1) selection or preparation of starting materials to ensure the desired purity and stoichiometry ranges; (2) definition of environmental conditions that will provide desired equilibria over the entire temperature range; and (3) provision of the desired temperature and temperature distribution in the growth zone.

#### A. Review of Literature

During the first quarter of this program a concentrated effort has been made to search the literature for pertinent information on the carbides of interest. Subjects sought include: melting point as a function of stoichiometry, single-phase composition range, lattice parameters as a function of composition, gaseous equilibria at high temperatures, carbide solubility in liquid metals, and appropriate ceramic forming conditions. Most of this information has been collected, and a summary of factors pertinent to this investigation will be presented in the next quarterly report.

#### B. Crystal Growth Studies

##### 1. Melt Growth

When materials melt congruently, without decomposing, and without undergoing phase changes below the melting temperature, melt growth offers the greatest potential for producing pure, large single crystals at reasonable growth rates. Ideally, in all modifications of this general technique, the melt is maintained slightly above the melting point under equilibrium conditions, while the crystallizing solid is held just below the melting temperature. Once growth is completed, the crystal is cooled to room temperature under conditions that minimize thermal gradients through the crystal, in order to minimize residual stress levels.

During this program the Verneuil modification of melt growth will be applied to the carbides of tantalum and hafnium. Two heat sources will be studied in order to establish relative advantages and disadvantages. One is an r-f plasma<sup>1</sup> and the other is a two- or three-phase a-c arc.

The r-f plasma is uniquely suited for Verneuil crystal growth in that it provides a large-diameter, low-velocity plasma ball which, by suitable manipulation, can simulate the geometry of the combustion flame employed in conventional flame-fusion processes. The temperatures attained in the plasma region, however, are sufficient to melt the most refractory materials. Since the r-f plasma is electrodeless, it can be operated on chemically reactive gases such as hydrogen or various hydrocarbons without corrosion of the device or contamination of the growing crystal.

The r-f oscillator to be employed in this work is a 20-kw, tuned-grid, tuned-plate unit constructed at Stanford Research Institute. During the first quarter of this program, effort was directed toward optimizing plasma stability over extended time periods by modifying the oscillator design. Several systems were explored, including tuned-grid, tuned-plate and Hartley circuits. The system finally selected was a tuned-grid, tuned plate circuit incorporating an inductive coupling to the load circuit and a variable tuning capacitor in the load circuit. This has resulted in an extremely efficient and stable operating mode. Power output can be controlled by varying the load capacitance, and the operating frequency can be shifted over several megacycles if the operating gases require special tuning of the oscillator.

Immediately below the plasma will be a resistance-heated carbon tube furnace operating as near the carbon-carbide eutectic temperature as possible. This furnace will be employed to maintain the desired temperature distribution during growth as well as to permit crystals to be cooled slowly at completion of a run.

Another heating technique which appears quite promising for this application is a-c arc-melting. This technique has been used in Europe recently for growth of electrically conducting oxide crystals. For this program, it is possible that carbon electrodes may be suitable. If not, carbide tips may be provided either as inserts or as metal-reaction coatings. Furnaces permitting the use of two- and three-phase arcs for Verneuil crystal growth have been designed and are being constructed.

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<sup>1</sup> Reed, T. B., Induction-Coupled Plasma Torch, J. Appl. Phys. 32, 821 (1961)

In considering fusion of the refractory carbides, attention must be directed toward composition control in the gas phase. Frequent reference appears in the literature to the loss of carbon from refractory carbides at elevated temperatures. For this reason it is essential that some provision be made for increasing the carbon partial pressure in the vicinity of the growing crystal. On the other hand, great care must be taken not to cause carbon deposition in cooler regions of the furnace. Carbon deposits on the plasma tube, for example, would lead to shorting and destruction of the furnace chamber. Thus, although the crystal will tend to reach equilibrium with its surroundings during the extended growth period, the entire system is dynamic, and thermodynamic considerations can only serve as an effective guide to experimental studies.

A brief investigation was conducted during this period to consider the equilibria and kinetics among gases used to introduce carbon (e. g.,  $\text{CH}_4$ ,  $\text{C}_2\text{H}_2$ ,  $\text{C}_2\text{H}_4$ ,  $\text{CCl}_4$ ) and their decomposition products (e. g., solid carbon and gaseous molecules,  $\text{H}_2$ , etc.). For application to the growth of carbide crystals, it was considered that we must maintain a concentration of gaseous carbon species approximately equal to that in the vapor of the carbide. Hoch<sup>2</sup> determined the vapor pressure of carbon (actually, this is for the  $\text{C}_1$  gaseous species) above graphite, tantalum carbide, and tungsten carbide. His results indicate that the vapor pressure of carbon over tantalum carbide is only about 10 percent of that over graphite.

The most stable gaseous species containing carbon at temperatures below  $3300^\circ\text{K}$  is acetylene. At the temperatures of interest, acetylene will decompose to produce some carbon and a considerable amount of hydrogen. Thus, at  $3000^\circ\text{K}$ , under equilibrium conditions, more than about 10 percent acetylene in hydrogen may cause carbon deposition. If a metastable state can be maintained, about 95 percent acetylene can be employed. Pure acetylene should not deposit carbon at  $4000^\circ\text{K}$  or above. A number of experimental determinations will be required to establish the applicability of these calculations under crystal growth conditions.

When carbon arcs are employed for heating, rather than the r-f plasma, a quite different set of environmental conditions may be required to maintain desired carbide stoichiometries. In this case, a considerable carbon vapor pressure may be present in the vicinity of

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<sup>2</sup> Hoch, M., P. E. Blackburn, D. P. Dingley, and H. L. Johnston, The Heat of Sublimation of Carbon, J. Chem. Phys. 59, 92 (1955)

the growing crystal. Again, owing to the nonequilibrium conditions existing in the crystal growing furnace, experimental studies will be required to establish appropriate environmental compositions.

## 2. Solution Growth

Another method of crystal growth which appears well suited to preparation of the refractory carbides of tantalum and hafnium is growth from solution in liquid metal alloys. By this method crystal constituents may be transported at relatively low temperatures, greatly simplifying temperature control problems and inert container requirements. In addition, the possibility of greatly reducing defect densities and deviations from theoretical stoichiometries by growth at low temperature is most attractive.

The feasibility of growing these carbide crystals will be explored by using the Institute's existing techniques and furnace.<sup>3</sup> No experimental work on solution growth has been initiated as yet. As mentioned, the Institute is constructing a second solution crystal growth furnace in order to obviate studying the growth of several compounds having widely differing characteristics in one furnace, and the contamination that would occur under such conditions. The second furnace should be placed in operation during the month of July, and crystal growth studies will be initiated at that time.

The technique to be employed will be to melt a low-melting alloy of the refractory metal (Ta or Hf) and a non-carbide-forming metal, capable of dissolving a significant quantity of the carbide, in a graphite crucible that will serve as the source of carbon. The melt will be equilibrated isothermally in the temperature range 1500 to 1900°C and will then be moved into a thermal gradient position to cause crystals to nucleate and grow in a selected region of the melt. Crystals will be removed from the alloy by leaching with an appropriate acid.

Work to date has been directed toward searching the literature in order to establish suitable compositions for initial study. The first experimental work will be concentrated on establishing conditions to provide material transport and the growth of polycrystalline carbide.

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<sup>3</sup> Halden, F. A., Growth of Silicon Carbide Crystals from Solution in Molten Metal Alloys, Silicon Carbide, A High Temperature Semiconductor, Pergamon Press, 1960, p. 115



Following this, solubility measurements as a function of temperature may be made in the range of interest in order to provide the information required in order to attempt to control the limit nucleation.

#### IV FUTURE WORK

It is anticipated that the following progress will be made during the next report period.

1. Construction of the first plasma and arc furnaces will be completed and melting studies will be initiated.
2. Determinations will be made of the quantities of hydrocarbon gases which can be introduced into the furnaces without soot formation, and work will start on measurement of the effect of these gases on carbide stoichiometry.
3. The new solution crystal growth furnace will be placed in operation and studies will be started to obtain carbide polycrystalline growth.